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參展科別 化學

作品名稱 **PVA unveiled the actual role of starch in the Briggs-Rauscher reaction**

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關鍵詞 **PVA、Briggs-Rauscher reaction、oscillation**

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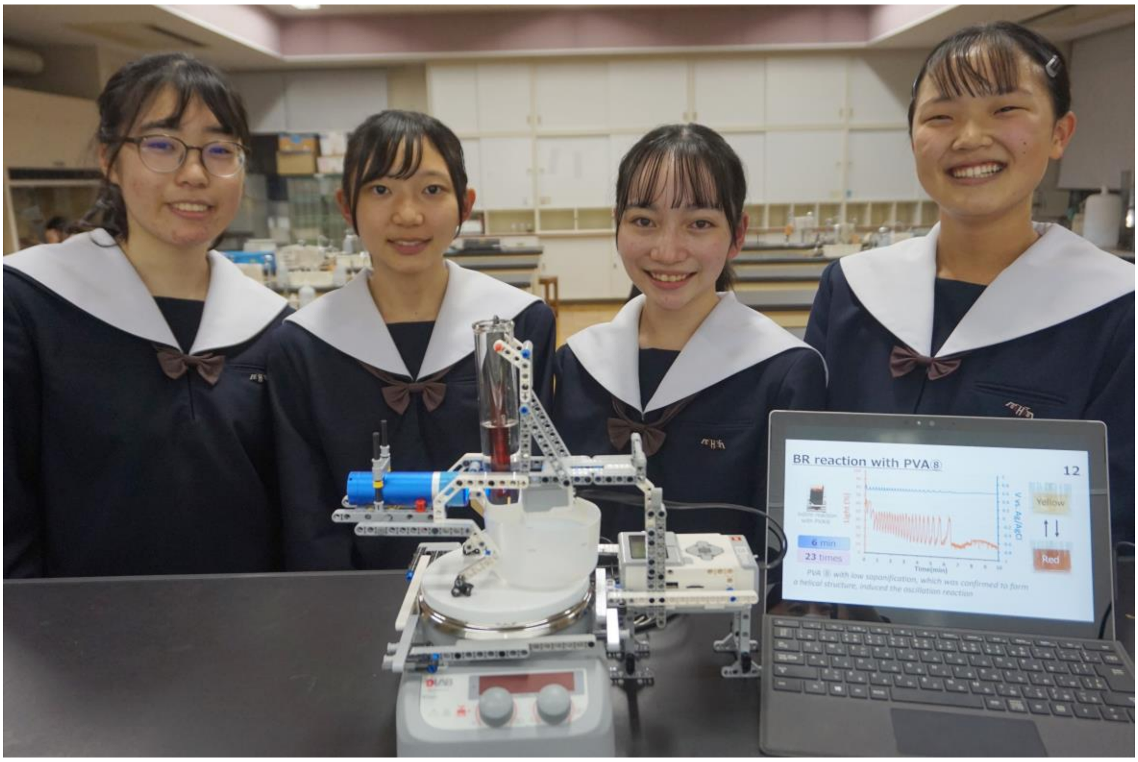

1. Background and the purpose of this study

The Briggs Rauscher reaction (BR reaction) is one of the famous oscillating reactions; the aqueous mixture of KIO_3, H_2SO_4, H_2O_2, $C_3H_4O_4$, $MnSO_4$, and starch exhibit color change between yellow and blue-purple repeatedly. The blue-purple color formation is due to the iodine test reaction caused by inclusions of polyiodides such as I_3^- and I_5^- in the helical space of starch[1]. Although starch added in the BR reaction has been considered to be just an indicator to make the purple color solution, our seniors found that the oscillations do not continue in the absence of starch[2]. They hypothesized that starch's linear helical framework is necessary to elongate the lifetime of the oscillating reaction.

Our initial interest was not the study of the BR reactions but the study of slime. Slime is a gel-like toy, a mixture of borax and laundry starch that contains poly(vinyl alcohol) (PVA) as the main component. Our literature search found that PVA forms a helical structure and then exhibits the iodine reaction like starch[3]. We thought PVA might be useful to verify the senior's hypothesis, so we studied the BR reaction with laundry starch used for preparations of slime; however, contrary to our expectations, the BR-type oscillation was not observed.

The literature search also showed that when PVA ($[CH_2CH(OH)]n$) is prepared from poly(vinyl acetate) ($[CH_2CH(OAc)]n$ (Ac = acetyl group)) by saponification, the properties of the products are largely dependent on the saponification degrees. The products, ($[(CH_2CH(OH))x(CH_2CH(OAc))y]$), are commonly called PVA. It is known that the water-soluble polymers have helical and non-helical structures in aqueous solutions depending on the saponification degrees[4]. If the helical structure of the starch is intrinsic for the elongation of the lifetime of the BR reaction, only PVA with helical structures will cause similar behavior.

The first purpose of this research is to clarify the relation between PVA's structure and PVA-I_2 color reaction. The second is to clarify the actual role of starch in the BR reaction. We studied the effects of using PVA solutions with different saponification degrees and viscosities and explored the role of the helix structure in the BR reaction.

2. Method

Reagents used for the general BR reactions are listed in Table 1[5]. In the general BR reactions, starch is added as the reagent D, and in this study, PVA shown in Table 2 is added instead of starch as D'. We detected the color and voltage changes of the reaction solution by using a photosensor of the LEGO MINDSTORM and Ag/AgCl reference electrodes. The equipment used for our research is shown in Fig. 1.

Table 1 Reagents for the general BR reaction

	Reagents	mmol	mol/L	mL
A	KIO_3	4.4	6.9×10^{-2}	22
	H_2SO_4	1.2	1.9×10^{-2}	
B	H_2O_2	25	3.9	20
C	$C_3H_4O_4$	3.1	4.8×10^{-2}	10
	$MnSO_4$	0.7	1.1×10^{-2}	10
D	Starch	--	(1 %)	2.0
D'	PVA	--	(3.7 %)	2.0
D'''	Indicator	--	5.0×10^{-3}	0.2

Table 2 Characteristics of PVAs for our experiments

Sample Number	Saponification Degree mol/%		Viscosity mPa・s	Degree of Polymerization
①			3.2 - 3.8	300
②	High	(98.0 - 99.0)	25.1 - 31.0	1,700
③			54.0 - 66.0	2,400
④	Medium	(95.5 - 96.5)	24.0 - 30.0	1,700
⑤			3.2 - 3.6	300
⑥	Low	(87.0 - 89.0)	27.0 - 33.0	2,400
⑦			40.0 - 48.0	2,400
⑧	Low	(79.0 - 81.0)	29.0 - 35.0	2,000

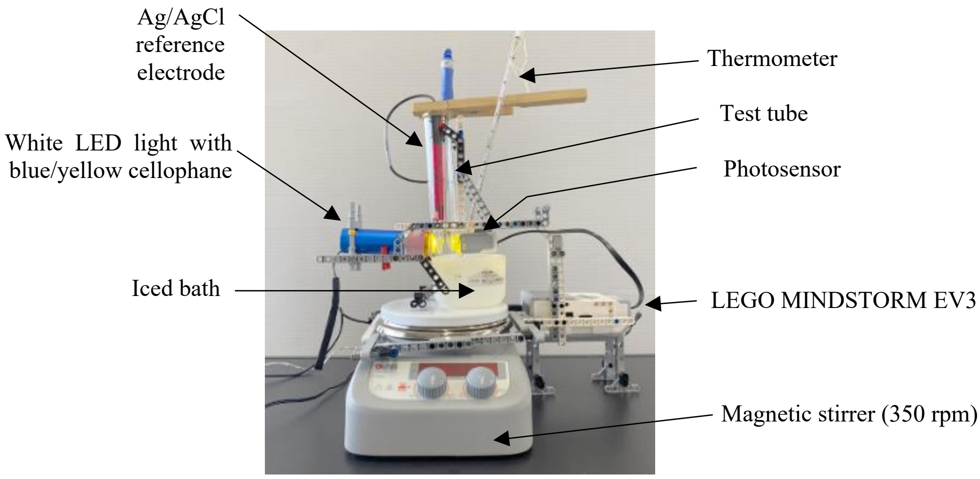

Fig. 1 Equipment for measurement of BR reaction

3. Result and Discussion

3-1: Correlation between structural features of PVA and iodine color reaction

We prepared eight PVAs with various saponification degrees and viscosity shown in Table 2 and added the iodine solution (0.010mol/L, 200μL) into each PVA solution (3.7%, 5mL). Then, we measured the absorption (ABS) spectra of each solution (Fig.2). We used three cells whose light path length is 1.0 cm, 0.10 cm, and 0.20 cm in measuring ABS spectra. But the charts of Figs are shown after normalizing the absorbances to the case that we used the cell with the light path length of 1.0 cm.

Although PVA ①～③ didn't show the color changes, PVA④～⑧ showed the color changes to red. The peaks of 300~350 nm are based on I_3^- in the iodine solution[6], and that of 500nm is ascribed to the I_3^- in the helical structure of PVA (PVA⊃I_3^-). For the peak around 500nm, the lower the saponification degrees, the higher the absorbance intensity. These results suggest that PVA ①～③ with high saponification don't have the helical structure, and PVA⑤～⑧ with low saponification have the helical structure. PVA④ with medium saponification might have a helical structure partially because this PVA showed a weak peak around 500 nm. We also studied the correlation between viscosity and the iodine color

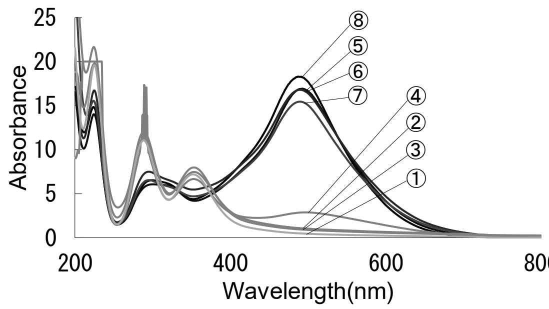

Fig.2 ABS spectra of PVA-iodine color reaction solutions

reaction activity, but no relation was observed.

3-2: Iodine color reaction of PVA with boric acid

For the next study, we researched the iodine color reaction of PVA with boric acid because we found that some literature[7)8)] says that boric acid would make the helical structure of PVA much stronger. We added boric acid aqueous solution (4.0%, 1.0 mL) and iodine solution (0.010 mol/L, 200 μL) into each PVA①～⑧ solution (3.7%, 5.0 mL). Then, we heated the solutions to dissolve the sediment, measured each sample's ABS spectra after cooling, and found that PVA①～③ showed blue before heating, while PVA④～⑧ showed red. After heating, all samples changed the color to yellow, then after cooling, PVA④～⑧ returned to the initial color, but PVA①～③ didn't; the color became slightly blueish yellow. Fig.3 shows the ABS spectra of the iodine color reaction of PVA with boric acid. Compared Fig.3 to Fig.2, it is obvious that the peaks at around 500 nm of PVA④～⑧ with low saponification degree were weakened. These results suggest that the structure of (PVA⊃I_3^-) is decreased by adding boric acid. On the other hand, the charts of PVA①～③ with high saponification showed almost the same peaks as Fig.2.

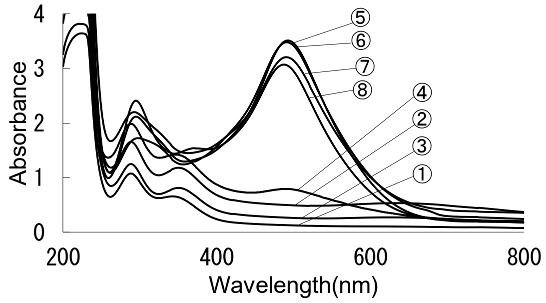

Fig.3 ABS spectra of iodine color reaction of PVA with boric acid

Although adding boric acid didn't make the helical structure stronger, we confirmed that PVA①～③ showed the blue color before heating. This color is different from the iodine color reaction of PVA④～⑧. It suggests that adding boric acid to PVA①～③ can form another structure that traps I_3^-, which is different from the helix structure.

3-3: The activity of Iodine color reaction of PVA with various concentrations of boric acid

From experiment **3-2**, PVA①～③ with high saponification formed the blue solution by adding boric acid. To clarify this phenomenon, we measured the ABS spectra of PVA① aq. solution treated with various concentrations of boric acid (Fig.4). We found that the addition of a higher concentration of boric acid changed the solution color from yellow to blue. The color change is reflected by the appearance of the strong peak at around 700nm. While a peak at around 500 nm in Fig.3 was assigned to the absorption by the helical PVA that includes I_3^- (PVA⊃I_3^-), we believe that a peak that appeared at around 700 nm is the result of the formation of a zeolite-like PVA-boric acid which has a three-dimensional framework that traps I_3^- (PVA-boric acid⊃I_3^-).

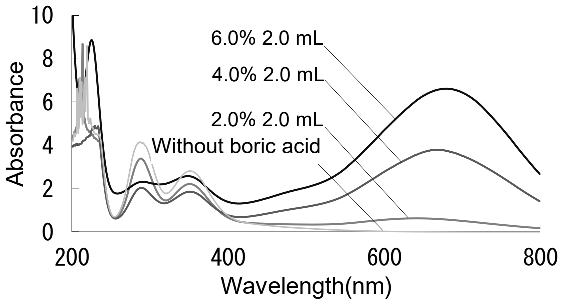

Fig.4 Iodine color reaction of PVA① with various concentrations of boric acid

3-4: Measurements of BR-type oscillations with PVA

In the general BR reaction using starch, reagents listed in Table 1 are added in the order of A, C, D, B; the oscillation continued for about 6 minutes, consisting of about 22 oscillations. As mentioned above, our seniors showed that only a poor oscillation in voltage was observed for the BR reaction without starch.

Our initial attempts to generate the BR reaction using PVA in laundry starch were unsuccessful. But we retried the creation of BR-type oscillations using PVA, which was confirmed to have a helical framework instead of starch. For solutions including helical PVA, we prepared two solutions, 2.0 mL of 3.7 % of PVA ⑤ and ⑧. For solutions including 3D helical PVA, we prepared 1.0 mL of 3.7 % of PVA① solution with 1.0 mL of 4.0 % of boric acid aq. solution. As a control experiment, 2.0 mL of 3.7 % of PVA①, which does not have a helical structure, was also prepared.

The result of PVA①, which doesn't have a helical structure, showed five oscillations in voltage, but we could not find the color changes(Fig.5). This behavior is similar to the BR reaction carried out without starch. It is confirmed that a solution using PVA having no helical structure causes no or poor BR reaction. Although the PVA①-boric acid solution showed the iodine test reaction, PVA①-boric acid did not show the BR reaction either. Currently, we think that the PVA-boric acid structure would be collapsed by contact with reagents A, B, and C, which are acid, oxidant, and reductant.

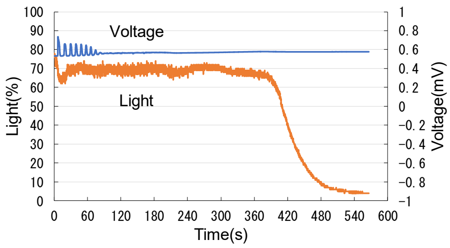

Fig.5 Observed oscillation of the BR reaction that PVA① was added instead of starch

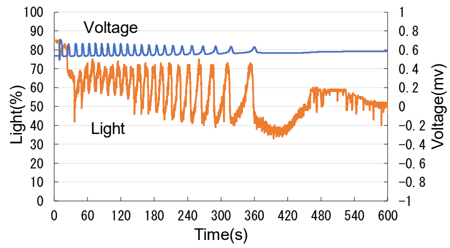

Fig.6 Observed oscillation of the BR reaction that PVA⑧ was added instead of starch

On the other hand, for the solutions using PVA⑤ and ⑧, which have a helical structure, the color repeatedly changed between red and yellow, and the voltage also changed responding to the color change. The oscillation continued for 6 minutes, consisting 20 oscillations for PVA ⑤ and 23 oscillations for PVA⑧. They were almost the same results as the general BR reaction with starch. These results clarify that the helical structure of starch or PVA is essential to elongate the oscillations of the BR reaction. This is the first example of the BR reaction carried out using PVA.

3-5: Measurements of BR-type oscillations with PVA and Ferricyanide

Furthermore, we found that the addition of $K_3[Fe(CN)_6]$ (0.0050 mol/L, 200 μL), which has a high redox activity, in the BR reaction solution with PVA⑧, drastically elongated the lifetime (50 min) and increased the oscillations times (95 oscillations) (Fig.7). This result suggests that the oxidation-reduction reactions by the ferricyanide ion promote the redox process of iodine and iodide ions. Interestingly, the results of the BR-type oscillation with starch and ferricyanide (Fig.8) were almost the same as the reaction with PVA⑧. These results demonstrate that PVA⑧ with a helical structure plays a similar role as starch in the BR reaction, indicating that the co-existence of the compounds with helical structures is essential for proceeding the BR reaction.

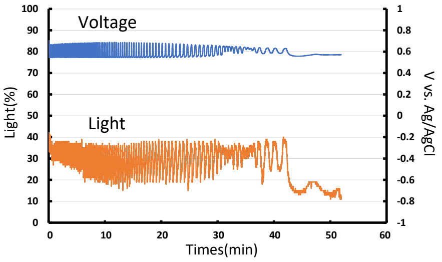

Fig.7 Observed oscillation of the BR reaction with PVA⑧ in the presence of ferricyanide

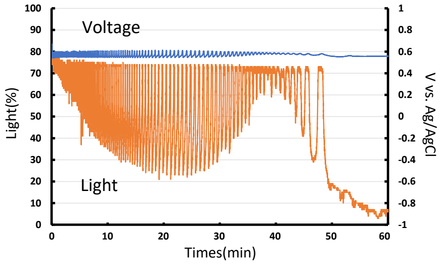

Fig.8 Observed oscillation of the BR reaction with starch in the presence of ferricyanide

4. Conclusion

First, we studied the iodine color reaction behaviors for various PVA solutions, exhibiting that PVA with low saponification forms helical structures and shows the iodine color reaction, which creates red colored solutions. On the other hand, PVA with high saponification degree did not show the reactivity.

Second, we found that adding the helical-structured PVA to the reaction solution instead of starch induces the BR-type oscillating reaction. This is the first example of the oscillating reaction using PVA. The oscillation that lasted for 6 minutes with 23 oscillations was almost the same as the general BR reaction using starch. On the contrary, additions of PVA having no helical structure induced only a few numbers of oscillations.

Moreover, we found that the addition of $K_3[Fe(CN)_6]$ in the solutions of the BR reaction with PVA elongated the lifetime of the oscillations significantly. The behavior is also similar to the BR reaction using starch. These results demonstrate that the helical structures of the starch and PVA are essential components for proceeding and elongation the lifetime of the BR reaction.

5. Further investigation

We would like to explore the effect of the saponification degree, the viscosity, and the polymerization degree of PVA on the oscillating time and number.

6. Acknowledgment

This work was carried out by four members. We would like to comment that Ms. Rina Tsurumi has participated as the essential coworker who equally contributed to the work. And we also would like to thank Kuraray and Prof. Kondo of Shizuoka University.

7. References

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Very increasing work.

The color changing in starch and PVA solution are different. In starch is blue, and in PVA is deep brown. If possible, you can look further into these phenomena. Is it due to the helical structure or interaction between the helical structure and I3- species？